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Processing and Characterization of a New Biodegradable Composite Made of a PHB/V Matrix and Regenerated Cellulosic Fibers

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In this study, a biodegradable composite consisting of a degradable continuous cellulosic fiber and a degradable polymer matrix—poly(3-hydroxybutyrate)-co-poly(3-hydroxyvalerate (PHB/V with 19% HV)—was developed. The composite was processed by impregnating the cellulosic fibers on-line with PHB/V powder in a fluidization chamber. The impregnated roving was then filament wound on a plate and hot-pressed. The resulting unidirectional composite plates were mechanically tested and optically characterized by SEM. The fiber content was 9.9 ± 0.9 vol% by volumetric determination. The fiber content predicted by the rule of mixture for unidirectional composites was 13.8 ± 1.4 vol%. Optical characterization showed that the fiber distribution was homogeneous and a satisfactory wetting of the fibers by the matrix was achieved. Using a blower to remove excess matrix powder during processing increased the fiber content to 26.5 ± 3.3 vol% (volumetric) or 30.0 ± 0.4 vol% (rule of mixture). The tensile strength of the composite parallel to the fiber direction was 128 ± 12 MPa (10 vol% fiber) up to 278 ± 48 MPa (26.5 vol% fiber), compared to 20 MPa for the PHB/V matrix. The Young's modulus was 5.8 ± 0.5 GPa (10 vol% fiber) and reached 11.4 ± 0.14 GPa (26.5 vol% fiber), versus 1 GPa for the matrix.

KEY WORDS: Processing; biodegradable composite; biodegradable polymers; PHB/V; regenerated cellulosic fiber.

INTRODUCTION

The use of biodegradable polymers contributes to reduce actual waste and environmental problems, but these materials still suffer from high production costs. Reinforcement with biodegradable cellulosic fibers would improve the mechanical properties of the biopolymers and increase their range of applications, and thus, such a composite will be worth its higher price and will be totally biodegradable. This type of composites undergoes the compound's polar incompatibility induced by the hydrophylic (polar) character of cellulose and the hydrophobic (nonpolar) one of the synthetic polymers [1, 2]. Potential applications are seen in the field of energy and impact absorption, where a weak interfacial shear strength is advantageous (sport protection articles, bicycle helmets [3], bumpers for light cars). Increased composite interfacial shear strength would allow its application for structural elements and eventually allow it to compete, after redimensioning of the parts, with high-performance composites: internal parts of vehicles [4], sport articles, transport containers, and special packaging. Other specialty domains are medical applications [5, 6] and as osteosynthesis plates (e.g., Refs. 7 and 8). A previous study showed poor homogeneity of the fiber distribution in the unidirectional composite and poor fiber–matrix adhesion [3]. In this study, a processing method for a totally biodegradable composite consisting of a poly(3-hydroxybutyrate)-co-

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poly(3-hydroxyvalerate) polymer matrix (PHB/V) and of a high-crystalline regenerated cellulosic fiber is proposed. Both matrix and fibers are manufactured from renewable resources, and both undergo sustainable development. A filament winding process, which can be highly automated, was used. Cellulosic fibers are intensively investigated as fiber or reinforcement material for conventional thermoplastics [4, 9–15] or even for PHB or PHB/V [2, 16]. In this work, regenerated fibers are used instead of native fibers. The proposed composite degrades biologically in the presence of bacteria or fungi [17, 18]. PHB/V degradation occurs mainly through enzymatic hydrolysis, as simple hydrolysis in water is very slow [19, 20].

EXPERIMENTAL

Materials

The cellulosic fiber was regenerated and assembled in rovings of 1000 or 500 filaments. While the mean filament diameter was 12.4 μm, scanning electron microscopy measurements showed that the standard deviation of the undried filament diameter was ± 0.58 μm ($n = 66$), due to the elliptical shape of the filament cross section. The surface was not treated. Fiber density was 1.52 g/cm^3 and crystallinity was about 60% (WAXS measurement). Tensile strength and elastic modulus of the used cellulosic fiber were 1400 MPa and about 36 GPa, respectively. Numerous hydroxyl groups are responsible for the hydrophilic behavior of cellulose.

The PHB/V (Biopol; [21]) copolymer used contained 19.1% hydroxyvalerate (HV). The density of hot-pressed plates, measured in a water bath, was 1.2196 ± 0.0005 g/cm^3 (1.25 g/cm^3 for injection-molded samples and 0.28 g/cm^3 for powder [22]). The modulus of elasticity of samples cut in the plates was 1 GPa, and the tensile strength 20 MPa [3]. The melting temperature is 151°C. It is a thermoplastic polyester with a mainly aliphatic character. The high HV content is expected to give the copolymer a suitable elongation at break ($\epsilon_B = 27\%$) to match the required elongation at break for a matrix in a composite: $\epsilon_{B(Matrix)} \geq 3\ \epsilon_{B(Fiber)}$ [23].

Methods

Processing

The composite was manufactured on-line with the following realized processing unit (Fig. 1).

(1) The first module is the fluidization chamber (1), where the roving is impregnated at room temperature with PHB/V powder (particle diameter of 600 nm). A six-blade propeller, optimized for this application, has a diameter of 25 cm and is spun close to the bottom of a cylindrical chamber (17-cm height and 29-cm diameter) at 310 rotation/min, so that PHB/V powder fills the whole chamber volume. The density of the powder in the fluidization chamber is between 16 and 33 g/L. The powder particles stick to the roving due to electrostatic forces.

(2) A blower is used to remove the superfluous biopolymer powder in order to increase the fiber-to-powder ratio. The blower had a propeller diameter of 6 cm and the voltage can be varied between 0 and 12 V.

(3) Subsequently, the powder is sintered onto the roving in an 80-cm-long heat channel (3), where the temperature reaches 270°C in the middle (retention time,

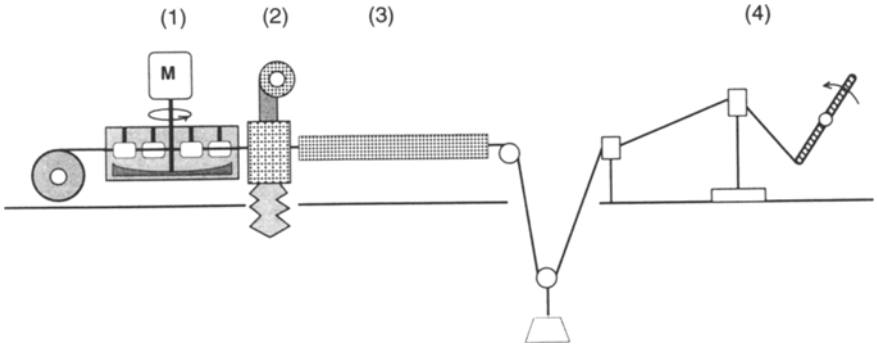

Fig. 1. The on-line manufacturing process of the biodegradable composite: a cellulose roving is impregnated with powder matrix in a fluidization chamber (1). The fiber content is increased by removing superfluous powder with a blower (2). The biopolymer powder is then fixed to the fiber in a heat channel (3) and the filaments are wound on a plate by a winding machine (4).

4 s). Since winding fibers on a plate result in discontinuous speed, the roving is driven through a compensation section, located between the sintering and the winding modules.

(4) The winding machine pulls the preimpregnated roving through the process unit at a speed of ca. 20 cm/s and winds the impregnated roving on a plate with the dimensions 30 × 30 × 2 cm. One border of the plate is mounted with springs which are compressed by screws during the winding process. The screws are then released to stretch the filaments on the plate. Winding at different angles and shapes is possible.

Table I shows the different process parameters. The settings were optimized in preliminary tests. The prepregs were then hot-pressed according to the cycle described in Fig. 2.

Two types of unidirectional plates were manufactured (Table II). Sample types A and B were processed into a single layer with a roving of 1000 filaments. To manufacture plates C and D, a roving of 500 filaments was used, with four layers being wound on the plate.

Determination of Fiber Content

The method of the carbonization of one composite's compound could not be employed, since the carbonization temperatures of matrix and cellulosic fibers are very close. Attempts to dissolve the thermoplastic matrix in a solvent were not successful because biopolymer residues could still be found after 3 days in dichlormethane. Therefore, the following method was used.

Volumetric. During the winding process, the lateral distance between two prepreg rovings on the plate

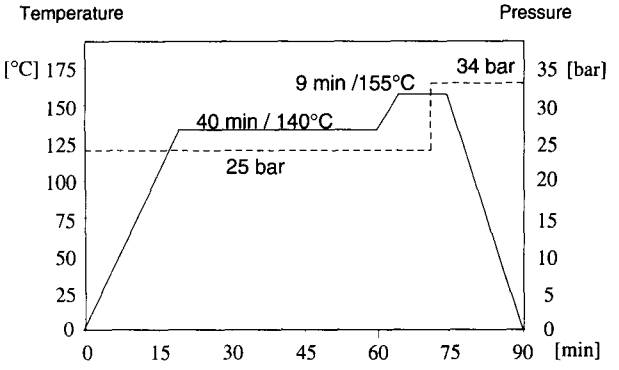

Fig. 2. Temperature and pressure cycles to consolidate the prepregs.

was set at 1.44 mm, which corresponds to the powder-impregnated roving width (d). Using the thickness of each sample (t), the volumetric fiber content (V_f/V_c) can be determined (vol%). In Eq. (1), W and L indicate the prepreg width and length, l is the number of layers, f is the number of filaments per roving, and r is the filament mean radius. Indices are as follows: c, composite, f, fiber; and m, matrix.

$$V_f = \frac{w}{d} lf(\pi r^2)L \tag{1}$$

so that

$$\frac{V_f}{V_c} = \frac{(w/d)\, lf(\pi r^2)L}{WLt} = \frac{lf(\pi r^2)}{dt} \tag{2}$$

Porosity. Measurements on the sample volume (V_c) include its porosity (index, p). Weight determinations (M_c) exclude the air content so that the porosity can be determined [Eq. (3)].

Table I. Process Parameters of the Prepreg: Optimization by Optical Appearance Regarding Homogeneity of Powder Distribution Inside the Roving

Module	Setting	Range investigated	Chosen setting
Fluidization chamber	Powder density	16–13 g/L	~25 g/L
	Propeller blade number	2–6	6
	Propeller surface	50–250 cm^2	250 cm^2
	Number of guiding rolls	2–6	6
Blower	Rotations per minute	200–500	310
	Voltage	0–12 V	Off or ~10 V
Heat channel	Temperature	270°C	270°C
	Retention time	2–5 s	4 s
	Covering of the channel	Open or covered	$\frac{2}{3}$ covered
Winding machine	Roving tension	100–1000 g	100–1000 g
	Roving speed	10–25 cm/s	20 cm/s

Table II. Hot-Pressed Plate Types and Tensile-Tested Composite Samples ($N = 6$ for Densities and $n \geq 10$ for Weight and Thickness)

Plate type	Tensile sample	Filament roving (f)	Layer quant. (L)	Blower	Sample quantity	Weight [g]	Thickness (t) [mm]	Density [g/cm^3]
A	0°	1000	1	Off	18	2.16 ± 0.19	0.86 ± 0.07	1.237 ± 0.004
B	90°	1000	1	Off	10	2.13 ± 0.02	0.83 ± 0.02	1.237 ± 0.004
C	0°	500	4	On	10	1.69 ± 0.07	0.63 ± 0.02	1.272 ± 0.01
D	90°	500	4	On	10	1.54 ± 0.13	0.6 ± 0.05	1.272 ± 0.01

$$V_c = V_p + V_f + V_m \quad \text{and}$$
$$M_c = M_f + M_m = \rho_f V_f + \rho_m V_m$$

give

$$V_p = V_c - \frac{M_c - \rho_f V_f}{\rho_m} - V_f \tag{3}$$

Mechanical Testing

From each composite plate, tensile samples were die cut into standard dumbbell shapes according to DIN 53 455, shape number 3, and tested accordingly. The thickness and weight of each sample were measured. The orientation of the fibers in the tensile samples was either 0 or 90°. Descriptions of the samples tested are summarized in Table II. The nominal strain rate used was 0.2%/min (10 mm/min) for tensile strength determinations and 0.44%/min for elastic modulus measurements. The tensile tests were performed between 5 and 15 days after hot pressing.

With the rule of mixture [Eq. (4)] it was possible to predict the modulus of elasticity of the composite in function of the fiber volume content [24]. With V_f/V_c from the measured fiber content, the elastic modulus of the composite could be calculated.

$$E_c = \frac{V_f}{V_c} E_f + \left(1 - \frac{V_f}{V_c}\right) E_m \tag{4}$$

RESULTS AND DISCUSSION

Density of the manufactured biocomposite (Table II), measured in deionized water, was 1.237 ± 0.004 g/cm^3 for plates A and B and 1.272 ± 0.01 g/cm^3 for types C and D. Samples C and D were thinner and lighter because they had less matrix due to the action of the blower.

Fiber Content

Because the roving was homogeneously wound on the plate, and the prepreg was minimally spread out by the hot-pressing process, Eq. (1) can be applied to the whole hot-pressed plate as well as to each tensile sample. The projected surface area ($W \cdot L$) of the die-cut tensile test samples was 2083 ± 12 mm^2.

In Table II, the volume of the fibers was 174.69 ± 17.3 mm^3 in samples A and B and 349.37 ± 34.7 mm^3 in samples C and D. In further calculations (Table III), standard deviations were considered for all measurements except for the number of filaments in a roving, the distance between two rovings, the density of fibers, and the elastic modulus of fiber and matrix.

The volumetric method applied to the type A and B plates gave a fiber volume content of 10 vol% (Table III). This fiber content is low for a composite material, as 60 vol% is generally considered optimal for continuous filaments [25]. The fiber–matrix ratio will have to be improved in future studies.

The fiber volume content could be significantly increased by removing part of the biopolymer powder with the blower. The fiber volume content increased from about 10 vol to 26.5 ± 1 vol% as measured volumetrically. The blower design and power range still remain to be optimized in order to get the highest possible fiber content.

Table III. Fiber Content and Porosity of the Tested Samples (Statistics Are of ≥ 10 Measurements)

Plate type	Blower	Volumetric (vol%)	Porosity (vol%)
A	Off	9.9 ± 1.8	3.1 ± 1.6
B	Off	10.1 ± 1.1	2.6 ± 2.3
C	On	26.5 ± 3.3	2.2 ± 1.2
D	On	28.1 ± 5.0	5.5 ± 1.2

The porosity of the samples was low, and not dependent on the fiber content (Table III). No pores could be observed on the fracture surface of the composite by SEM, so that porosity was probably situated in the interface. The mean measured porosity, which varied between 2.2 and 5.5 %, may be reduced by a better vacuum during the hot-pressing process.

Comparison of Tensile Properties

At about 10 vol% fiber content (Table IV), the tensile strength of the composite parallel to the fiber was 128 ± 12 MPa, in contrast to 20 MPa for the PHB/V matrix. The elastic modulus was 5.8 ± 0.5 GPa, versus 1 GPa for the matrix only.

The tensile strength parallel to the fibers of samples containing about 27 vol% fibers increased to 278 ± 48% MPa. The modulus of elasticity increased as well and reached 11.4 ± 0.14 GPa.

The composite showed a slightly higher elastic modulus than the theoretical modulus for 0° samples, as described by the rule of mixture [Eq. (4)] in Fig. 3. Therefore, either the fiber content of the composite was, higher than measured (13.8 ± 1.5 vol% without the blower or 30 ± 0.4 vol% with the blower set on 10 V) or the elastic modulus of the matrix of 1 GPa was underestimated. Holmes gives a modulus of elasticity ≥1.2 GPa for a PHBV with 19% HV [8]. The determination of the modulus of elasticity of the matrix alone was performed with melt-cast tensile samples, as hot-pressing was not applicable. Thus, the morphologies of the matrix in the composite and in the bulk were inevitably different. It is known that fibers may act as nucleation centers for the polymer melt [27].

The samples tested 90° to the fiber orientation showed low tensile properties, which were due partially to the die-cut process. In the 10-mm-wide tensile test samples, 1 mm on each side seemed, by optical observation, to be delaminated, resulting in earlier sample failure. Additionally, the porosity of the composite as well as inhomogeneities in the fiber distribution also affect the tensile strength. Optimization of some processing parameters, such as blower power, powder density in the fluidization chamber, and interfacial adhesion, should improve these results.

Table IV. Table Properties of the Different Manufactured Biocomposite Plates[a]

Plate type	Fiber orientation	Fiber content (vol%)	Modulus of elasticity (GPa)	Tensile strength (MPa)	Elongation at break (%)
A	0°	9.9	5.8 ± 0.5	128 ± 12	3.4 ± 0.2
B	90°	10.1	1.6 ± 0.1	11 ± 2	1.4 ± 0.7
C	0°	26.5	11.4 ± 0.14	278 ± 48	4.3 ± 0.4
D	90°	28.1	1.2 ± 0.4	3.3 ± 1.1	0.1 ± 0.2
	Regenerated cellulosic fiber		35.7	1392	5.98
	PHB/V matrix		1	20	27
	Reg. cellul. fiber (35 vol%)-PHB/V		5.9-7.3	440-470	5.2-8.3
	Reg. cellul. fiber (65 vol%)-epoxy		22-28	525-600	2.2-3
	Jute (32.9 wt%)-epoxy		15.042	104	—
	Jute (21.8%)-polyester		12.21	84	—
	Flax (19 wt%)-PP		16	136	—
	Choir (9 wt%)-polyester		4.045	18.61	—
	Cotton fabric-polyester		2.76-4.14	34-690	—
	Banana fabric (11 wt%)-polyester		3.33	35.92	—
	Flax (19 wt%)-PP		16	136	—
	Glass fiber-epoxy		20-47	900-1100	2-4
	Carbon fiber-epoxy		20-160	Up to 1700	0.5-1.8

[a] At least 10 samples were tested. The test speed was 10 mm/min, or 2 mm/min for elastic modulus measurements of samples C and D. Mechanical properties of the fiber and PHB/V matrix and comparison with other unidirectional fiber-reinforced composites [3, 24, 30-32].

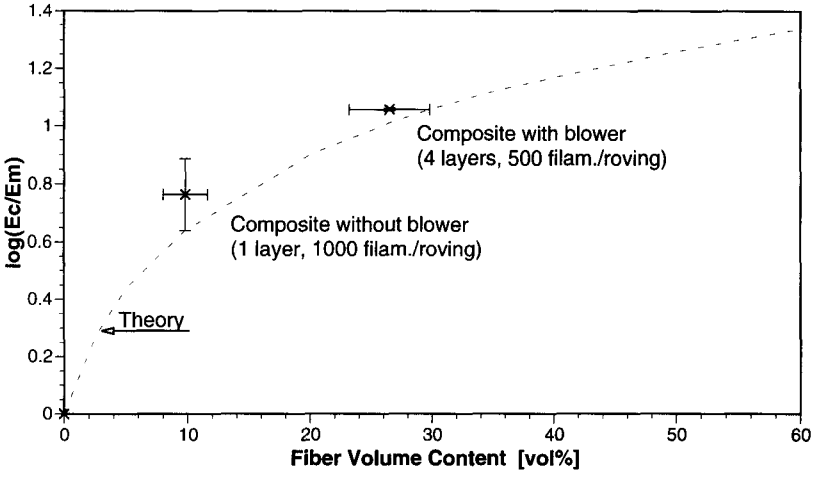

Fig. 3. Comparison of the measured fiber volume content (volumetrically) with the theoretical fiber content, obtained by the rule of mixture applied to the elastic modulus of the composite.

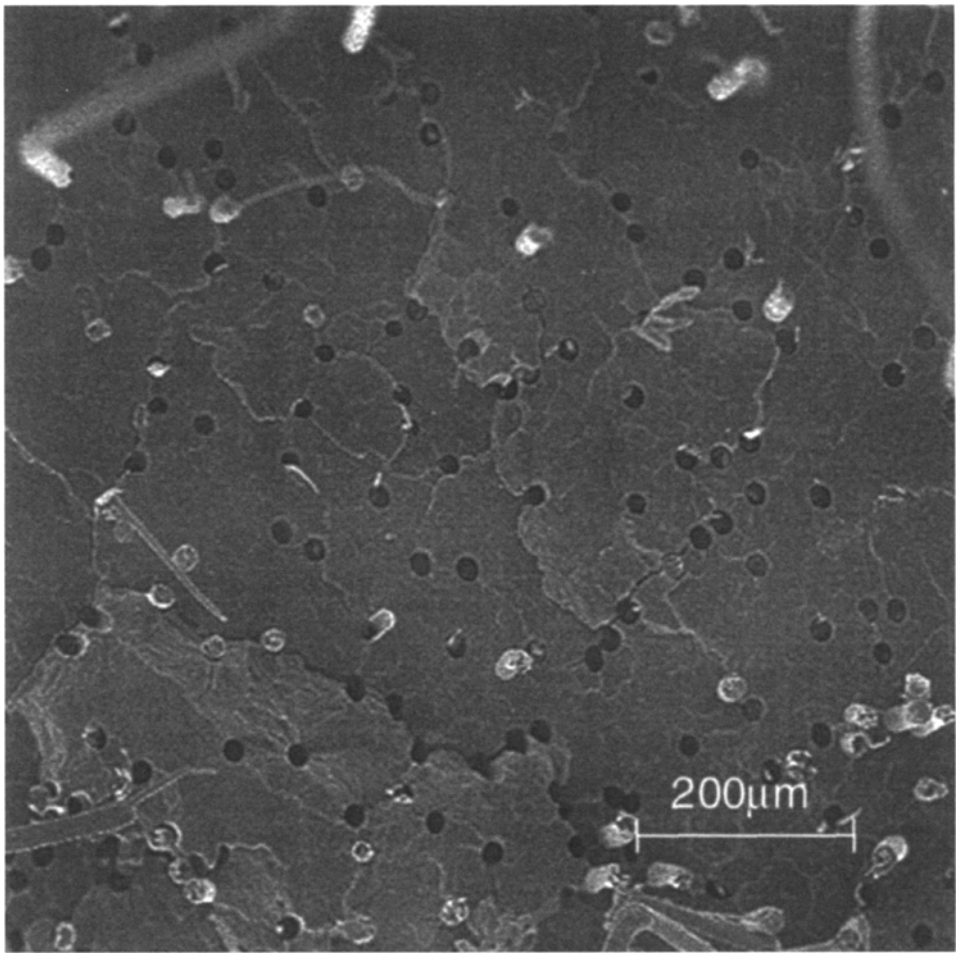

Fig. 4. SEM image of the tensile fracture surface of the biodegradable composite (type A, 0° fiber orientation) shows a homogeneous fiber distribution and a low fiber volume content.

Fiber Distribution, Wetting, and Interfacial Adhesion

Optical characterization of the tensile fracture surface by SEM showed that fiber distribution was significantly improved, compared to previous work [3]. Each filament was wetted with matrix and their distributions showed only slight variation (Fig. 4).

SEM images (Fig. 5) indicate a poor fiber–matrix adhesion because of the clean and smooth topography of fiber prints in the matrix. This was essentially due to the contrary surface characteristics of the hydrophilic fiber and the hydrophobic matrix. A weak interfacial shear strength is advantageous for energy and impact absorption but disadvantageous for load-bearing applications. The matrix between two fibers formed waved lips, indicating a tough behavior of the PHB/V matrix.

The samples with ~27 vol% fiber were investigated by light microscopy. From the observation of the fracture surface, it could be seen that the number of fiber pullout increased with the fiber content.

CONCLUSIONS

In contrast to previous studies [3], problems of insufficient wettability of the fibers by the matrix and inhomogeneity of the fiber distribution could be solved with the proposed processing unit. The biodegradable composite showed that a fiber content of about 27 vol% (volumetric determination) can be reached by optimizing the process parameters. The calculated porosity of the composite is comparable to conventional composites. Further optimization of the adhesion between cel-

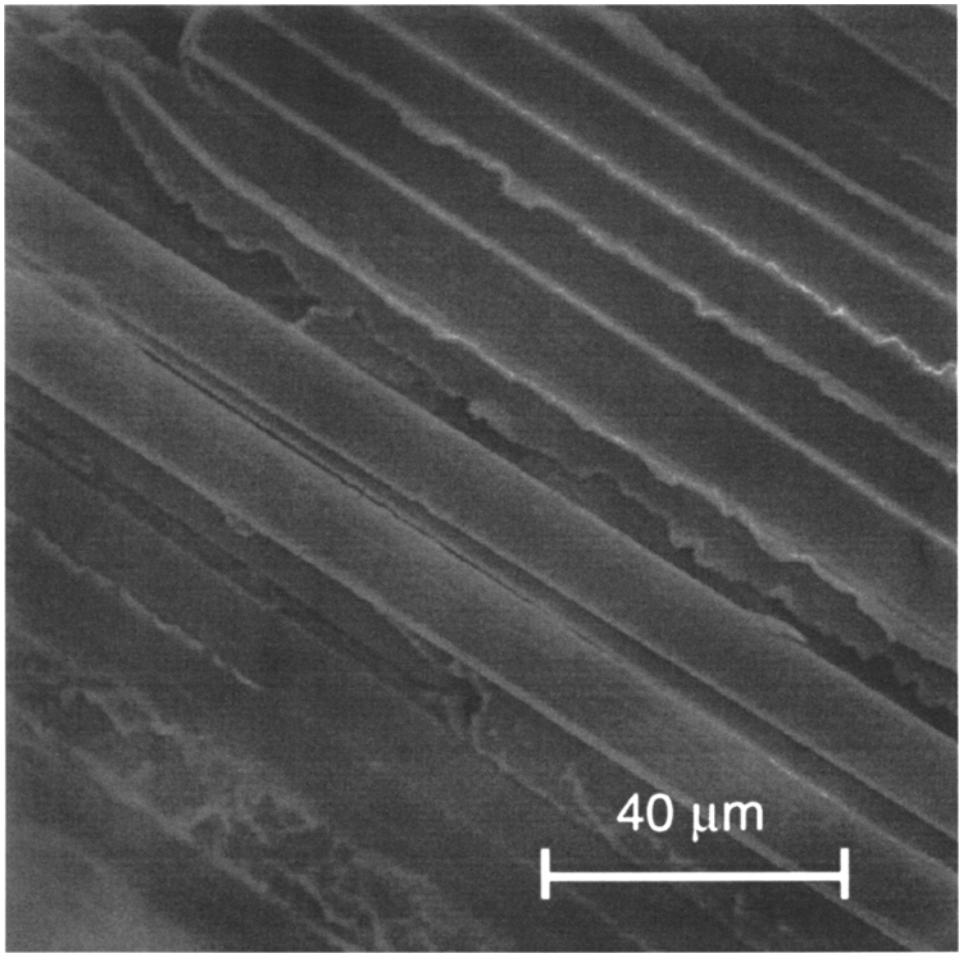

Fig. 5. SEM image of a fracture surface of the biodegradable composite (type B, 90° fiber orientation) shows good wetting of the fibers by the matrix. The smooth prints of the fibers indicate poor adhesion of the matrix to the fibers, while the waved lips indicate a tough behavior of the matrix.

lulosic fiber and PHB/V matrix is necessary. There is a wide variety of coupling agents or fiber surface treatments mentioned in the literature [4, 15, 16, 26, 28, 29], but their applicability and efficiency on regenerated cellulosic fibers remain to be seen. Poor interfacial adhesion, however is needed in applications where energy or impacts are to be adsorbed. Ongoing research is aimed at improving the adhesion between the fiber and the matrix, so that the biodegradable composite could benefit from an even wider application range.

The results demonstrate promising mechanical properties of the PHB/V-regenerated cellulosic fibers composite. As predicted by unidirectional fiber reinforcement theory, cellulosic fibers significantly increase the stiffness and strength of the PHB/V matrix while maintaining the biodegradability of this material.

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